

First-principles study of the ortho-KC₆₀ polymer

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We present results of first-principles band calculations as well as structural optimization of the orthorhombic KC₆₀ polymer. Our band dispersion is significantly *anisotropic*, and different from previous band calculations. The character of the conduction band is explained in terms of linear combinations of the molecular orbitals of I_h C₆₀ and a perturbation coming from the polymerization. [S0163-1829(98)05944-X]

I. INTRODUCTION

AC₆₀ (A = K, Rb, Cs) is known to have an orthorhombic polymer phase consisting of one-dimensional chains made of covalently connected fullerenes; two covalent bonds bridge the fullerenes forming a four-membered ring.¹ Due to the one-dimensional bridging geometry,¹⁻³ the electronic structures of these systems could be expected to be quasi-one-dimensional, and this has been supported by several experiments involving RbC₆₀ and CsC₆₀.^{2,4-6} However, theoretical band-structure calculations^{7,8} do not agree with these results. Local-density approximation (LDA) band calculations on the ortho-RbC₆₀ polymer were performed by Erwin *et al.*, resulting in a nearly isotropic band dispersion.⁷ The orientational configuration of the chains corresponding to the $I2/m$ space group was used in order to save on CPU cost. At the time of the calculations, this configuration differed from that of the $Pmnn$ model structure proposed from x-ray diffraction experiments.¹ Interestingly, however, a very recent x-ray experiment on the single crystals *o*-KC₆₀ and *o*-RbC₆₀ showed that *o*-RbC₆₀ does indeed belong to the $I2/m$ space group, while *o*-KC₆₀ belongs to the $Pmnn$ space group.^{9,10} Contrary to the results of Erwin *et al.*, the semiempirical tight-binding calculations of *o*-RbC₆₀ of Tanaka *et al.* using a $Pmnn$ unit cell showed a narrow but anisotropic band dispersion.¹¹ In a different paper, Tanaka *et al.* showed that the band dispersion is very sensitive to the orientational configuration of the chains,¹² suggesting an explanation for the difference between the isotropic band of Erwin *et al.* and the anisotropic band of Tanaka *et al.* However, these results do not seem to be consistent with a series of experiments that suggest that the $Pmnn$ polymer has a more anisotropic character than the $I2/m$ polymer does.^{2,4-6,9,10} In order to shed light on the present confusing situation, more detailed investigations are needed.

In this paper, we present a first-principles electronic structure study of the ortho-KC₆₀ polymer, and show how the electronic states of the conduction bands are related to its one-dimensional polymer geometry. Although electronic band-structure calculations of AC₆₀ have been reported by three other groups,^{7,8,11,12} to our knowledge this is the first quantitatively reliable calculation for the KC₆₀ polymer with a realistic atomic configuration, i.e., unit cell belongs to the $Pmnn$ space group and all atoms were allowed to relax without constraint.

II. METHOD

The calculations method is based on the density-functional theory¹³ within the local density approximation.¹⁴ Wigner's formula was used for the exchange-correlation potential.¹⁵ A plane-wave basis expansion and optimized pseudopotentials¹⁶ in separable form¹⁷ were adopted in this simulation. The total energy for a particular structure was calculated by utilizing the conjugate-gradient method¹⁸ to minimize the electronic degrees of freedom. Details of the calculations conditions will be discussed later.

III. RESULTS AND DISCUSSIONS

A. Optimized geometry

Structural optimization was performed on the KC₆₀ polymer, which has an orthorhombic unit cell containing two C₆₀ molecules and two K atoms. The cell parameters were fixed at the experimental values.¹ Initially, the C₆₀ molecules were placed at the body-centered positions, in which the atomic configuration of an isolated I_h C₆₀ molecule is used. We chose the initial orientational configuration of the fullerenes as the one proposed by Stephens *et al.*¹ The structural optimization was then performed without symmetry constraints. To obtain as precise a geometry as possible, we examined the convergency of the geometry as a function of the cutoff energy for plane waves ranging from 30 to 80 Ry with uniform sampling of either one (Γ) or four k points. The geometry was relaxed until all the forces acting on the atoms were less than 5×10^{-4} Hartree/au. Covalent bonds spontaneously appeared between the C₆₀ molecules during the optimization process, resulting in a one-dimensional chain structure. The calculated bond lengths of 1.62, 1.59, and 1.51 Å, for the C1-C1 interfullerene, the C1-C1 intrafullerene, and the C1-C2 or the C1-C3 bond lengths, respectively, are in agreement with the results of earlier theoretical calculations.¹⁹ They are also generally in agreement with the experiment.^{1,10} In the earlier experiment,¹ the C1-C1 intrafullerene distance was reported to be 1.74 Å, which is considerably longer than that determined theoretically, while, in the recent experiment,¹⁰ the C1-C1 distance is reported to be 1.55 Å, which is consistent with theoretical estimations.

As a result of the relaxation, there is distortion of the fullerene on a cross section normal to the chain. If we cut the fullerene on a plane normal to the chain, the cross section is

no longer a circle but an ellipsoid with diameters along the major and minor axes of 6.98 and 6.83 Å, a difference of about 2%.

Before moving on to a discussion of the electronic structure, we shall relate the geometry of the KC₆₀ polymer to the coupling of the conduction bands and the deformation of the C₆₀ molecule. It would be natural to speculate that the character of the lowest unoccupied molecular orbital (LUMO) states of isolated C₆₀ would be reflected in the conduction band. Therefore, we shall note the symmetry of the lowest unoccupied molecular orbital LUMO states of isolated *I_h* C₆₀. The LUMO states of the *I_h* C₆₀ molecule are threefold-degenerate *t_{1u}* states with *p*-like symmetry. The coordinate axes for these *p*-like (*t_{1u}*) states can be mapped onto the three orthogonal *C₂* rotational pivots of the *I_h* C₆₀ molecule. If we now go back to the calculated polymer structure, we note that the chain direction is parallel to one of the *C₂* rotational pivots, and the other two are parallel to the principal axes of the ellipsoidal cross section discussed above. Therefore, in this paper, we will take these three orthogonal directions as local coordinate axes for the *p*-like *t_{1u}* states as follows; the *z* axis is parallel to the chain direction, the *x* axis is parallel to the plane including the four-membered ring, the *y* axis is normal to the above two. We emphasize here that the ellipsoidal distortion may be plausibly associated with the Jahn-Teller effect; however, as will be clarified later in this paper, the relative positions of the *t_{1u}* levels in the polymer are instead determined by the crucial change in the local electronic states around the four-membered ring connecting the fullerenes.

B. Electronic structure

The electronic states of the orthorhombic polymer crystal were investigated using the first-principles band-calculations method. The householder diagonalization method with a plane-wave expansion was used to maintain the symmetry of the eigenstates as precisely as possible. In order to save on computational cost, the cutoff energy was reduced to 25 Ry, thereby reducing the number of basis functions to 25 000. We note here that the convergence of the band structure has been confirmed for both diamond and potassium crystals with this cutoff energy, though it is inadequate for structural optimization. Because the diagonalization of a matrix with a dimension of 25 000 requires a huge amount of CPU time even for the newer parallel supercomputers, we did not perform fully self-consistent diagonalization calculations but instead obtained the eigenvalues and the eigenstates through the following two steps. First, the effective potential for the Kohn-Sham equation was calculated self-consistently by means of conjugate gradient minimization of the total energy, in which 75 uniform *k* points in the first Brillouin zone were sampled. We then diagonalized the matrix calculated from the given effective potential.

The calculated band structure is shown in Fig. 1. First, we would argue the character of the conduction band. By examining the profiles of the lower six conduction bands along the Γ -*M* line, we can group the bands into pairs; the lowest and the third lowest, the second and the fourth lowest, and finally the fifth and the sixth lowest energy levels at the Γ point.

Direct inspection of the corresponding wave functions ensures the above categorization. We have examined the iso-

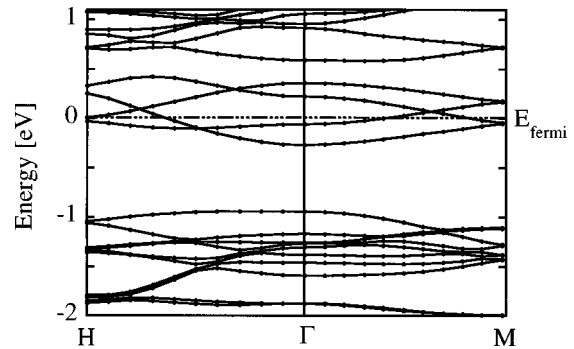


FIG. 1. Band structure of the ortho-KC₆₀ polymer. The Γ -*H* direction is parallel to the chain and the Γ -*M* direction is normal to the chain. The vertical axis denotes the energy in eV. The origin is placed at the Fermi level. Note: the Fermi level is not determined self-consistently; it is defined as the energy where the filling becomes half of the full occupation number during preparation of the effective potential by the conjugate-gradient method.

surfaces of these six wave functions at the Γ point. Those belonging to the lowest and the third lowest are displayed in Figs. 2(a) and 2(b), respectively. We can clearly see the bonding and the antibonding characters of the wave functions between the polymer chains. Furthermore, we can see the *t_{1u}* character surviving in these states, i.e., the π^* character of the C=C double bonds and the nodal plane, which includes the four-membered ring connecting the fullerenes. There is almost no evidence of hybridization with the other states. The *t_{1u}* symmetry and the bonding/antibonding characters as described above are also seen in the other four eigenstates, though the *t_{1u}* character in the sixth eigenstate is weakened; the second (Fig. 3) and the fourth lowest eigenstates at the Γ point have a nodal plane normal to the chain, while the fifth (see Fig. 4) and the sixth lowest eigenstates have a nodal plane normal to the above two nodal planes.

We can now understand that the wave functions of the conduction bands of the ortho-KC₆₀ polymer are, at least at the Γ point, linear combinations of the *t_{1u}* molecular orbitals (MO's) as follows,

$$\Psi_{p_i, \Gamma} = \frac{1}{\sqrt{2}}(\phi_{p_i} \pm \phi'_{p_i}), \quad i = x, y, z. \quad (3.1)$$

Here, ϕ_{p_i} and ϕ'_{p_i} denote the MO's belonging to the first and the second fullerenes in the unit cell, respectively. Note that the *x* axis of the first fullerene is taken to be parallel to the *y* axis of the second fullerene, since the coordinate axes of the *p*-like states for each fullerene have been taken independently so that the *x* axis includes the four-membered ring connecting the fullerenes. Due to the polymerization, the threefold degenerate *t_{1u}* states split into three different levels E_{p_x} , E_{p_y} , and E_{p_z} . These levels then constitute the interchain bonding/antibonding states, and the lowest state that has interchain bonding character will be occupied. Clear interchain bonding character can be seen in Fig. 2(a), where the interchain interaction is large enough to form a conduction band with three-dimensional dispersion.

We note here that the occupied levels associated with the four-membered ring connecting the fullerenes sink below the energy gap and so have not appeared in the above discus-

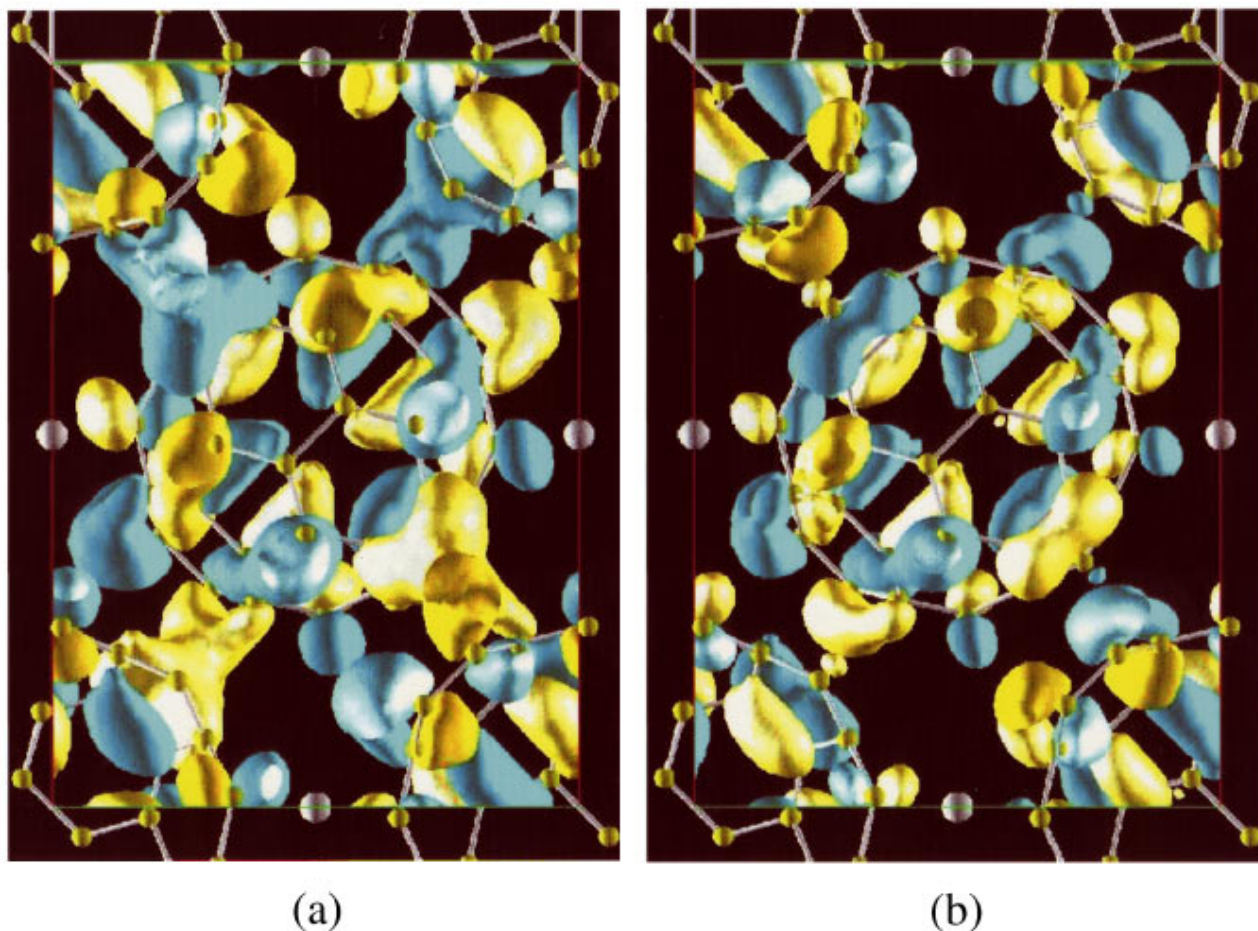


FIG. 2. (Color) The isosurfaces of the lowest (a), and the third lowest (b), eigenstate wave functions at the Γ point are drawn with the atoms represented by a ball and stick model in the orthorhombic unit cell. The yellow balls denote the carbon atoms, and the white balls denote the potassium atoms. The viewpoint is parallel to the chain direction. The isolevel is set to 1/5 of the maximum absolute amplitude. The yellow and the blue curved surfaces denote the isosurfaces of the positive and negative values of the wave functions, respectively.

sions. This may seem puzzling because alkali doping is known to be crucial to the synthesis of ortho-AC₆₀. Below, we argue as to how the formation of the covalent connections couples with the profile of the conduction band.

We now focus on the change in the local electronic states around the carbon atoms forming the four-membered ring. Due to the polymerization, the local electronic states are converted from sp^2 to sp^3 . This means that the σ^* and π^* states of the sp^2 rehybridize into the σ^* states of the sp^3 . We emphasize here that ϕ_{p_x} has an amplitude around the ring (see Fig. 4), while ϕ_{p_y} and ϕ_{p_z} do not. This means that only the levels that are functions of ϕ_{p_x} will be affected by the rehybridization. As can be seen from Fig. 1, the p_x band is lifted about 0.7 eV from the p_y - p_z band, and it forms a continuous band with the higher energy states.

To confirm the above scenario in which the rehybridization lifts only the E_{p_x} level, we have performed first-principles MO calculations on two different C₆₀ molecules having geometry equivalent to the polymer using GAUSSIAN94.²⁰ One is the bare C₆₀ molecule and the other is the C₆₀ molecule with the two carbon atoms that belong to the four-membered ring terminated with hydrogen bonds. In these calculations, Becke's 3 parameter hybrid method²¹ with Perdew's gradient-corrected correlation functional²² (B3P86)

and a 6-31G basis set were used. The bare deformed fullerene shows a too low E_{p_x} level, with $E_{p_x} = -4.6$ eV $< E_{p_z} = -4.2$ eV $< E_{p_y} = -4.1$ eV, while hydrogen termination serves to lift the E_{p_x} level, giving levels comparable to the band calculations, with $E_{p_z} = -4.0$ eV $< E_{p_y} = -3.9$ eV $< E_{p_x} = -2.9$ eV. Thus, we conclude that the formation of the four-membered ring connecting the fullerenes raises the p_x band from the continuous p_y - p_z band. In the latter MO calculations, the sequence $E_{p_z} < E_{p_y}$ is opposite to the Γ -point levels of our band calculations, but the difference is small in both cases. This is due to the crystal-field effect, which is observed as the difference in the strength of the interfullerene interaction; in $\Psi_{p_y, \Gamma}$, intrachain as well as interchain bonding character can be seen between the fullerenes, while no intrachain bonding character can be seen in $\Psi_{p_z, \Gamma}$ (see Fig. 3).

Finally, we would argue the dimensionality of the electronic structure. In *o*-RbC₆₀ and *o*-CsC₆₀, quasi-one-dimensional electronic properties were proposed from NMR and ESR experiments,^{2,4-6} while in KC₆₀ quasi-one-dimensionality has not been reported. Bommeli *et al.* suggested that *o*-KC₆₀ is an anisotropic, but not quasi-one-dimensional, strongly correlated metal,⁴ while Brouet *et al.*

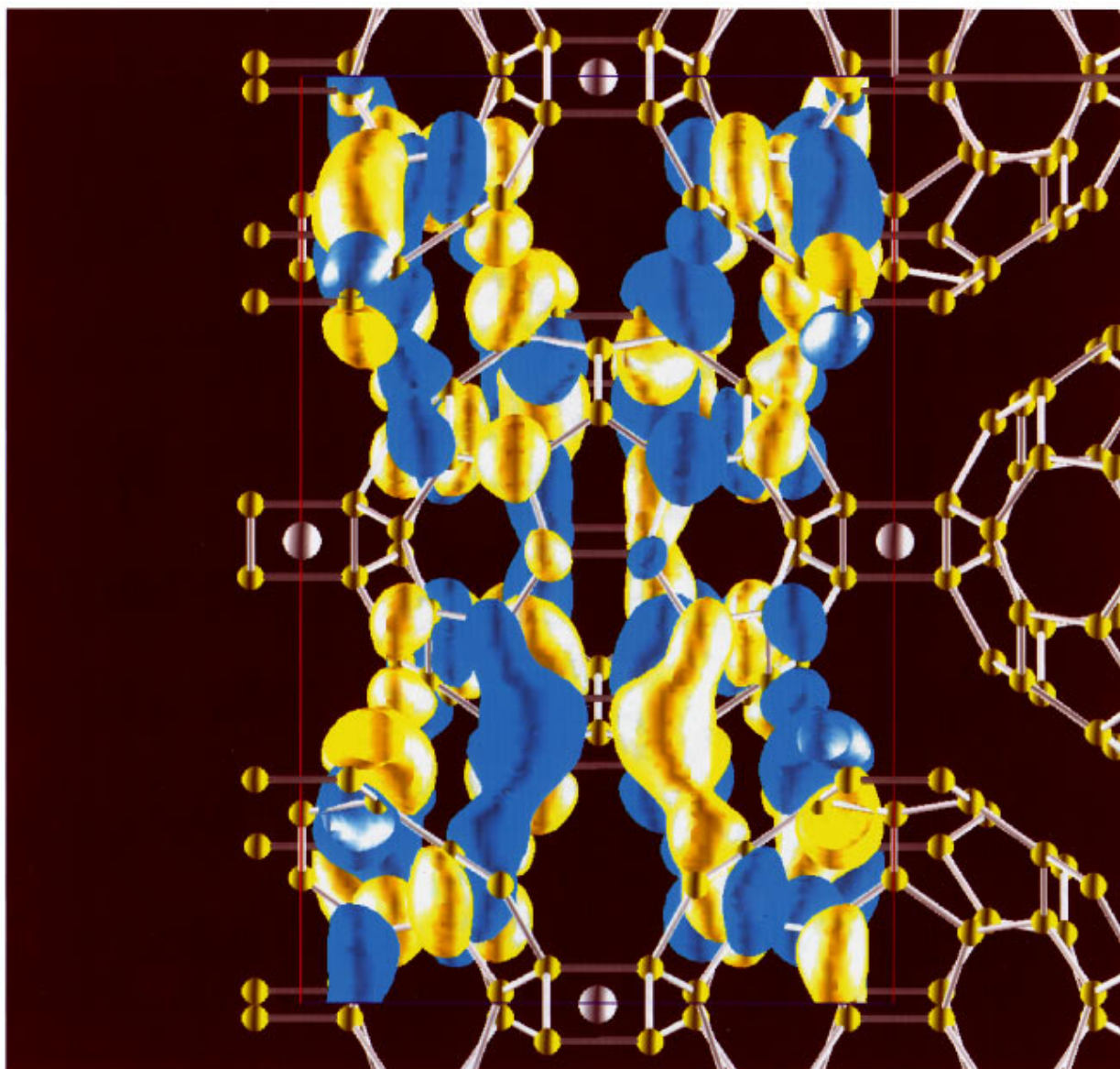


FIG. 3. (Color) The isosurfaces of the second lowest eigenstate wave function at the Γ point are drawn. The viewpoint is normal to the direction of the chain.

reported that it is an ordinary three-dimensional metal.⁵ The differences between *o*-KC₆₀ and *o*-RbC₆₀ (or *o*-CsC₆₀) could arise from a difference in the interchain separation, but there is now another possibility. Stephens *et al.* performed powder x-ray experiments and reported that the systems have nearly the same atomic configuration belonging to the same space group *Pmnn* but differing lattice parameters.¹ Very recently, though, Launois *et al.* performed single crystal x-ray diffraction experiments and reported that the space groups of these systems differ, *Pmnn* and *I2/m* for KC₆₀ and RbC₆₀, respectively.^{9,10} Launois *et al.* proposed that the differences in the electronic properties would come from the differences in the relative orientation for these two space groups.^{9,10}

Turning now to the theoretical side, LDA band calculations showed essentially isotropic electronic structures even for the *o*-RbC₆₀ *I2/m* unit cell,⁷ while an extended Hückel calculation gave a very narrow and anisotropic band dispersion.¹¹ Further, Shulte and Böhm performed semi-

empirical intermediate neglect of differential overlap (INDO) calculations, and they reported that the band structure is isotropic but the charge transfer energy is anisotropic.⁸

In our results, although the band dispersion along the Γ -*M* line (normal to the chain) in the lowest branch of t_{1u} band is not flat, it is considerably narrow, about 1/2 of that along the Γ -*H* line (parallel to the chain); the band structure is obviously anisotropic. Comparing our band structures with the previous ones, we see that the empirical tight-binding calculations by Tanaka *et al.*¹¹ gave a similar band structure along the Γ -*M* line, while the Γ -*H* dispersion was not fully represented by the simplified model Hamiltonian. Their band dispersion is very narrow, 0.1 eV, while our bandwidth has a considerably larger value of 0.5 eV. This is comparable with the LDA band calculations for the *o*-RbC₆₀ polymer by Erwin *et al.*, which utilized the local orbital method.⁷

The band structure of Erwin *et al.*,⁷ however, is significantly different from ours: in their band structure, the lowest

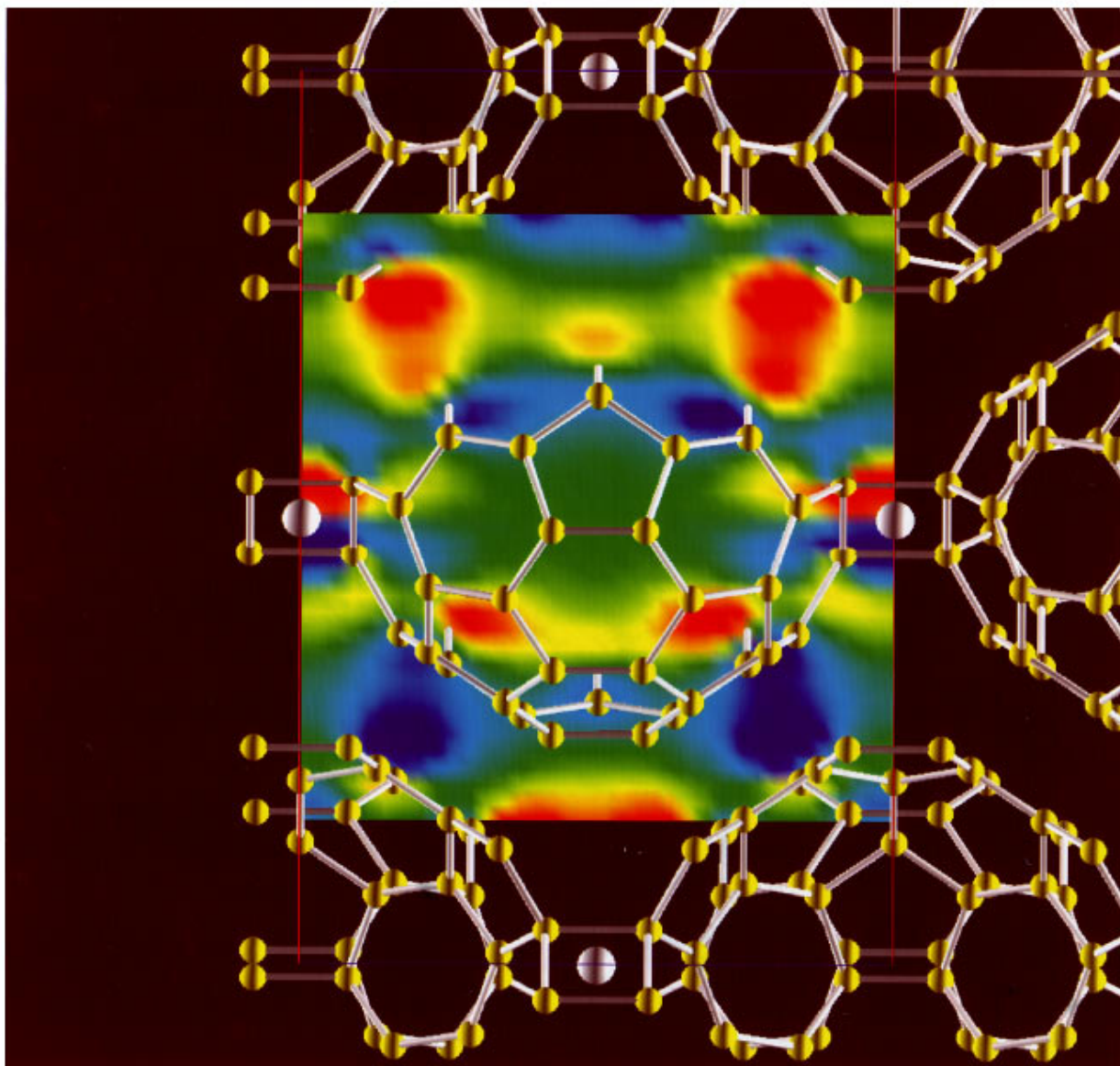


FIG. 4. (Color) A contour plot of the fifth lowest eigenstate wave function at the Γ point is drawn. The blue and red areas correspond to the negative and positive values of the wave function, respectively. The viewpoint is normal to the chain direction. The contour plane includes the four-membered ring connecting the fullerenes.

branch of the t_{1u} band is nearly isotropic in character. This may be due to their choice of the orientational configuration of the chains; they used a unit cell (space group $I2/m$) in which all the chains have the same orientation to save on CPU cost.⁷ This is different from an earlier experimental proposal for a structure belonging to the $Pmnn$ space group, in which the adjacent chains are rotated 90° from each other,¹ but it is close to that proposed by Launois *et al.*^{9,10} If we were to consider that the dispersion of the conduction band has been shown to be very sensitive to the orientation of the chains,¹² we may be able to understand why our band structure differs from the band structure of Erwin *et al.* However, from the viewpoint of anisotropy, the results of the band calculations show an opposite tendency in comparison with the experiment, where o -RbC₆₀ is more isotropic than o -KC₆₀. Also, a true comparison of the theoretical results may be obscured by the fact that different methods were used in the calculations. We therefore suggest that one should

compare band structures determined by exactly the same calculations method and level of optimization.

IV. CONCLUSION

We have performed semi-self-consistent-field LDA band calculations as well as first-principles geometry optimization of the ortho-KC₆₀ polymer. The resulting band has a three-dimensional but considerably anisotropic dispersion, different from previous band calculations.²³ We found that the lower six conduction eigenstates at the Γ point can be represented by linear combinations of the t_{1u} MO's. The rise of the p_x band is due to the sp^3 character around the four-membered ring connecting the fullerenes.

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- ²³We found another difference between our electronic structure and those of Erwin *et al.* (Ref. 7) or Tanaka *et al.* (Ref. 11). The character of the lowest branch in their results was Ψ_{p_z} , while it is Ψ_{p_y} in our calculations.